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Statistical Thermodynamics of an Anharmonic Oscillator

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In the present study we investigate the statistical thermodynamics of the anharmonic oscillator, whose energies are characterized by the potential $\frac{1}{2}x^2 + \lambda x^4$. Employing the energies recently obtained by Hioe and Montroll, we compute the partition function and the thermodynamic quantities for the anharmonic and quartic oscillators. Low- and high-temperature formulas are presented for the thermodynamic quantities of the oscillators.

KEY WORDS: Statistical thermodynamics; thermodynamic quantities; oscillator with positive anharmonicity; quartic oscillator.

1. INTRODUCTION

Problems in quantum field theory and molecular physics have led to the investigation of the properties of anharmonic oscillators characterized by the Hamiltonian

$$H(\omega, \lambda) = \tfrac{1}{2}(p^2 + x^2\omega^2) + \lambda x^4 \tag{1}$$

In the Schrödinger equation the associated energy levels and wave functions are solutions of

$$[(-\hbar^2/2m)(d^2/dx^2) + \tfrac{1}{2}m\omega^2 x^2 + \lambda' x^4]\psi = E'\psi$$

which for

$$E'/\hbar\omega = E, \qquad x = y/(m\omega/\hbar)^{1/2}, \qquad \lambda = \lambda'\hbar/m^2\omega^3$$

takes the form

$$[-\tfrac{1}{2}(d^2/dy^2) + \tfrac{1}{2}y^2 + \lambda y^4]\psi = E\psi \tag{2}$$

While previous attempts to solve Eq. (2) by perturbative and variational means[1] have not met with complete success, nonperturbative methods as

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introduced by Biswas *et al.*[2] have obtained iterative schemes for computing the energy eigenvalues of Eq. (2) for a restrictive range in λ. Recently, Hioe and Montroll,[3] by using the Bargmann representation of the Schrödinger equation, have developed rapidly convergent algorithms for arbitrary $\lambda\,(>0)$. Using a combination of computer evaluation of the resulting difference equations associated with Eq. (2) and a WKB type of analysis, they have derived various analytical formulas for certain regimes of λ and n.

In the present study, we take the energy eigenvalues $E_n(\lambda)$ (n being the quantum number of the energy eigenvalues) obtained from the Hioe–Montroll study and evaluate the thermodynamic quantities for the anharmonic and quartic oscillators. Since the energy eigenvalues are available for any (λ, n) regime, we compute the thermodynamic quantities for the general case of arbitrary temperature numerically. In particular, for small λ (<0.2) the heat capacity for low and high temperatures approaches that of the harmonic and quartic oscillators, respectively. However, for the large λ $(\geqslant 0.2)$ regime, the heat capacity approaches that of the quartic oscillator. Finally, for particular λ regimes explicit energy formulas are available for an arbitrary quantum number. Using these formulas, low- and high-temperature expressions are obtained for the thermodynamic quantities for the anharmonic and quartic oscillators.

2. THERMODYNAMIC QUANTITIES: GENERAL (λ, n) REGIME

The energy eigenvalues $E_n(\lambda)$ which are solutions of Eq. (2) can be characterized by two distinguishable regimes of λ and n. For small λ the energy levels are only slightly distorted from those of the harmonic oscillator, while for λ large the energy levels are only slightly altered from the quartic oscillator (with potential energy λx^4). One also finds for the small-λ regime that there is a transition from a harmonic to a quartic-like behavior of the energy for increasing quantum number. Having noted the dependence of the energy on λ and n, we now turn to examine the thermodynamics of the anharmonic oscillator.

From a knowledge of $E_n(\lambda)$ for all n, and the partition function Z, we can compute the thermodynamic quantities (free energy A, energy E, heat capacity C_v, entropy S) for the anharmonic oscillator. In this section we only present the results for the heat capacity since its behavior is representative of the other thermodynamic quantities. For $E_n(\lambda)$ expressed in terms of harmonic oscillator units (E rather than E' in Eq. (2) and $\beta = 1/kT$, with $T = T'/\hbar\omega$; β is dimensionless) Fig. 1 represents the heat capacity

$$\frac{C_v}{k} = \frac{1}{Z}\sum_{n=0}^{\infty}\left(\frac{E_n(\lambda)}{kT}\right)^2 \exp[-\beta E_n(\lambda)] - \left\{\frac{1}{Z}\sum_{n=0}^{\infty}\frac{E_n(\lambda)}{kT}\exp[-\beta E_n(\lambda)]\right\}^2 \tag{3}$$

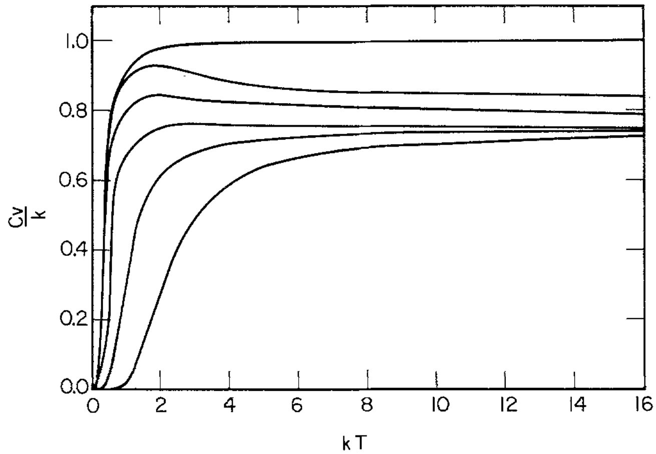

Fig. 1. Calculation of the heat capacity C_v/k vs. kT [Eq. (3)] for various λ. From left to right: 0, 0.01, 0.05, 0.5, 10, 100.

as a function of temperature for various values of λ. The energies have been taken directly from the Hioe–Montroll study [their equations (II.21)–(II.23), (III.7), (III.9), and (IV.16a)].[3] For small λ, one notes that the heat capacity behaves like the harmonic oscillator ($\lambda = 0$) while approaching the asymptotic value of three-quarters for the quartic oscillator at higher temperatures. Thus for low temperatures, the heat capacity as well as the energies of Eq. (2) are essentially those of the harmonic oscillator. At higher temperatures, the quartic-like energies from the higher quantum numbers are contributing to the partition function and as a result the heat capacity, as indicated in Fig. 1, tends asymptotically to the limit of the quartic oscillator.

The calculations above $\lambda = 0.2$ show the heat capacity for the anharmonic oscillator to be equivalent to the purely quartic oscillator in behavior. Again this result for $\lambda \geqslant 0.2$ is consistent with the dominance of the potential λx^4 in determining the values of the energy.

Having computed the general features of the thermodynamics of the anharmonic oscillator for arbitrary (λ, n) and temperature, we turn to the available explicit energy formulas and compute high- and low-temperature expressions for the anharmonic and the quartic oscillators.

3. THERMODYNAMIC EXPRESSIONS

For the anharmonic oscillator $\lambda \geqslant 0.2$ and quartic oscillator Hioe and Montroll have obtained explicit formulas for the energies of Eq. (2) for arbitrary n. However, for the anharmonic oscillator $\lambda \leqslant 0.2$ we only have explicit energy formulas for small n. We take these formulas and obtain expressions for the thermodynamic quantities at high and low temperatures. Finally we return and discuss the results of Fig. 1 in terms of these thermodynamic expressions.

The energy eigenvalues $E_n(\lambda)$ which are a solution of Eq. (2) for $\lambda \geqslant 0.2$ are[3]

$$E_n(\lambda) = \lambda^{1/3}(a_{1,n} + a_{2,n}\lambda^{-2/3} + a_{3,n}\lambda^{-4/3}), \qquad n = 0, 1$$

$$E_n(\lambda) = \lambda^{1/3}\left\{b_1\left[\left(n + \frac{1}{2}\right) + \frac{\delta}{n + \frac{1}{2}}\right]^{4/3} + b_2\left(n + \frac{1}{2}\right)^{2/3}\lambda^{-2/3} + b_3\lambda^{-4/3}\right\} \qquad n \geqslant 2 \tag{4}$$

where $b_1 = 1.376$, $b_2 = 0.26$, $b_3 = -0.0116$, $\delta = 0.02650$, and the $a_{i,n}$ ($i = 1, 2, 3$) are tabulated.[3] From a knowledge of the energies for the system we are now ready to obtain expressions for the partition function, more specifically on the form of the partition function and thermodynamic quantities at high and low temperatures.

In the high-temperature limit, the partition function Z may be taken as

$$Z = \sum_{n=0}^{\infty} \exp\left\{-\beta\lambda^{1/3}b_1\left[\left(n + \frac{1}{2}\right)^{4/3} + \frac{b_2}{b_1}\left(n + \frac{1}{2}\right)^{2/3}\lambda^{-2/3} + \frac{b_3}{b_1}\lambda^{-4/3}\right]\right\}$$

By introducing the new variable $\hat{n} = \beta^{1/2}[(n + \frac{1}{2})^{2/3} + c]$, where $c = (b_2/2b_1)\lambda^{-2/3}$ and taking $\beta < 1$, we can replace the above sum by the integral,

$$Z = (3/2)\beta^{-3/4}\{\exp[(-\beta/\lambda)\xi]\}\int_{\mu}^{\infty} [\exp(-b_1\lambda^{1/3}\hat{n}^2)]\hat{n}^{1/2}(1 - c\beta^{1/2}/\hat{n})^{1/2}\, d\hat{n}$$

$$\xi = b_3 - (b_2^2/4b_1), \qquad \mu = \beta^{1/2}[(1/2)^{2/3} + c] \tag{5}$$

By expanding (5) and integrating each term, we obtain an expression for the partition function which, when combined with appropriate thermodynamic formulas, yields the following expressions:

$$E = \frac{3}{4}\beta^{-1} + \frac{\xi}{\lambda} + \frac{\sqrt{b_1}}{4}\frac{\Gamma(1/4)}{\Gamma(3/4)}(\beta\lambda)^{-1/2} + O(\beta^{-1/4})$$

$$\frac{C_v}{k} = \frac{3}{4} - \frac{\sqrt{b_1}}{8}\frac{\Gamma(1/4)}{\Gamma(3/4)}\left(\frac{\beta}{\lambda}\right)^{1/2} + O(\beta^{3/4})$$

$$A = -kT\ln\left[\frac{3}{4}\beta^{-3/4}(b_1\lambda^{1/3})^{-4/3}\Gamma\left(\frac{3}{4}\right)\right] - \frac{b_1}{4\lambda} + \frac{\sqrt{b_1}}{2}\frac{\Gamma(1/4)}{\Gamma(3/4)}(\beta\lambda)^{-1/2} + O(\beta^{-1/4}) \tag{6}$$

$$\frac{S}{k} = \frac{3}{4} + \ln\left[\frac{3}{4}\beta^{-3/4}(b_1\lambda^{1/3})^{-3/4}\Gamma\left(\frac{3}{4}\right)\right] + O(\beta^{1/2})$$

in the limit as $\beta \to 0$.

At low temperatures we only consider the first two energy levels as contributing to the partition function; then the partition function takes the form

$$Z = 2\exp[-\beta E^{+}(\lambda)]\cosh[\beta E^{-}(\lambda)] \tag{7}$$

where $E_0(\lambda)$ and $E_1(\lambda)$ are from Eq. (4), and

$$\begin{aligned} E^{+}(\lambda) &= \tfrac{1}{2}[E_0(\lambda) + E_1(\lambda)] = \lambda^{1/3}(1.53 + 0.025\lambda^{-2/3} + 0.01\lambda^{-4/3}) \\ E^{-}(\lambda) &= \tfrac{1}{2}[E_0(\lambda) - E_1(\lambda)] = \lambda^{1/3}(-0.86 - 0.11\lambda^{-2/3} + 0.0026\lambda^{-4/3}) \end{aligned} \tag{8}$$

The thermodynamic quantities are then, for $\beta \gg 1$,

$$\begin{aligned} E &= E^{+}(\lambda) - E^{-}(\lambda)\tanh[\beta E^{-}(\lambda)] \sim E^{+}(\lambda) + E^{-}(\lambda) = E_0(\lambda) \\ C_v/k &= [\beta E^{-}(\lambda)]^2 \operatorname{sech}^2[\beta E^{-}(\lambda)] \sim [\beta E^{-}(\lambda)]^2 4\exp[2\beta E^{-}(\lambda)] \\ A &= -kT\ln\{\cosh[\beta E^{-}(\lambda)]\} - kT\ln 2 + E^{+}(\lambda) \sim E^{+}(\lambda) + E^{-}(\lambda) = E_0(\lambda) \\ S/k &= \ln Z + \beta\{E^{+}(\lambda) - E^{-}(\lambda)\tanh[\beta E^{+}(\lambda)]\} \sim 0 \end{aligned} \tag{9}$$

where the expressions on the right-hand side correspond to the limiting behavior of the quantities as $\beta \to \infty$. Comparison of Eqs. (9) with exact calculations (not shown here) of the thermodynamic quantities such as Eq. (3) have shown them to agree very well with these low-temperature expressions (i.e., through the C_v/k range 0–0.4). Equations (9) are general expressions for obtaining the low-temperature behavior of a system where $E^{+}(\lambda)$ and $E^{-}(\lambda)$ are defined.

For the anharmonic case of $\lambda < 0.2$, the only explicit energy formulas are for small n. Therefore we restrict our discussion of this λ regime to that of low temperature. Again if we consider the partition function to be expressed in terms of the first two energy levels, then from Eqs. (7) and (9),

$$\begin{aligned} E_0(\lambda) &= \frac{1}{2} + \frac{3}{4}\lambda - \frac{3}{2}\lambda^2\left(\frac{3}{2 + 9\lambda} + \frac{1}{4 + 30\lambda}\right) \\ E_1(\lambda) &= \left(1 + \frac{1}{2}\right) + \frac{15}{4}\lambda - \frac{15}{2}\lambda^2\left(\frac{2.5}{2 + 15\lambda} + \frac{1}{4(2 + 21\lambda)}\right) \end{aligned} \tag{10}$$

and with $E^{+}(\lambda)$ and $E^{-}(\lambda)$ appropriately defined as in Eq. (8),

$$\begin{aligned} E^{+}(\lambda) &= 1 + (9/4)\lambda - (3/4)\lambda^2 d^{+}(\lambda) \\ E^{-}(\lambda) &= -1/2 - (6/4)\lambda + (3/4)\lambda^2 d^{-}(\lambda) \end{aligned} \tag{11}$$

we have the description of the thermodynamic behavior of the anharmonic oscillator for $\lambda < 0.2$ at low temperature.

Before discussing the expressions in Eqs. (6) and (8) in terms of the results of Fig. 1, we next evaluate the high- and low-temperature formulas for the quartic oscillator since we have seen in our discussions of Fig. 1 that the anharmonic behavior goes over to that of the quartic oscillator at high temperatures.

The energy levels for the quartic oscillator with potential energy λx^4 are[3]

$$E_n(\lambda) = \lambda^{1/3} b_1[(n + 1/2) + 0.0265(n + 1/2)^{-1}]^{4/3}, \qquad n \geqslant 2$$
$$E_0(\lambda) = 0.667\lambda^{1/3}, \qquad E_1(\lambda) = 2.39\lambda^{1/3} \tag{12}$$

for all $\lambda > 0$.

As before we are only interested in the forms of the expressions for the partition function and the thermodynamic quantities at low and at high temperatures.

For high temperatures the partition function is

$$Z = \sum_{n=0}^{\infty} \exp[-\beta b_1(n + \tfrac{1}{2})^{4/3}]$$

We can replace the sum by an integral by introducing the variable $\hat{n} = \beta^{1/2}(n + 1/2)^{2/3}$, such that for $\beta < 1$

$$Z = (3/2)\beta^{-3/4} \int_{\mu}^{\infty} [\exp(-b_1\lambda^{1/3}\hat{n}^2)]\hat{n}^{1/2}\, d\hat{n} \tag{13}$$

From Eq. (13) the thermodynamic quantities as $\beta \to 0$ are

$$\begin{aligned} E &= (3/4)\beta^{-1} + [b_1^{1/2}/2\Gamma(3/4)](\lambda/\beta)^{1/2} + O(\beta^{3/4}) \\ C_v/k &= 3/4 + O(\beta^{3/4}) \\ A &= -kT\ln[(3/4)(b_1\lambda^{1/3})^{-3/4}\beta^{-3/4}\Gamma(3/4)] \\ &\quad + (4/3)[(b_1\lambda^{1/3})^{3/4}/\Gamma(3/4)]\beta^{-1/4} + O(\beta^{3/4}) \\ S/k &= 3/4 + \ln[(3/4)\beta^{-3/4}(b_1\lambda^{1/3})^{-3/4}\Gamma(3/4)] + O(\beta^{3/4}) \end{aligned} \tag{14}$$

The low-temperature expressions for the quartic oscillator are the same as Eqs. (7) and (9) except that we replace $E_0(\lambda)$ and $E_1(\lambda)$ by Eqs. (9) and

$$E^+(\lambda) = 1.53\lambda^{1/3}, \qquad E^-(\lambda) = -0.86\lambda^{1/3} \tag{15}$$

Having obtained thermodynamic expressions for the anharmonic and quartic oscillators at high and low temperatures, we now discuss these results in terms of the calculations of Fig. 1. From the analysis of the heat capacity for low temperatures one finds from Eqs. (9) and the appropriate $E^+(\lambda)$ and $E^-(\lambda)$ that for $\lambda < 0.2$ the limiting form of the heat capacity is

$$C_v/k \simeq \beta^2 e^{-\beta} g_h \tag{16}$$

where g_h is the correction term to the harmonic oscillator [here we have taken $E^-(\lambda = 0) = -\frac{1}{2}$ and $g_h = 1$, harmonic reference] and for $0 \leqslant \lambda \leqslant 0.2$,

$$g_h = [1 + 3\lambda - \tfrac{3}{2}\lambda^2 d^-(\lambda)]^2 \exp[-\beta(3\lambda - \tfrac{3}{2}\lambda^2 d^-(\lambda))] \tag{16a}$$

noting for $\lambda = 0$ that $g_h = 1$. Thus the heat capacity for the small λ (<0.2) regime is shown, as in Eq. (16), Fig. 1 and in the characteristics of the energy eigenvalues,[3] to involve corrections to the harmonic oscillator. However, for $\lambda \geqslant 0.2$ the heat capacity (low temperatures) has the limiting form

$$C_v/k \simeq \beta^2(2.96)\lambda^{2/3}\{\exp[-\beta\lambda^{1/3}(1.72)]\}g_q \tag{17}$$

where here g_q is the correction term to the quartic oscillator [$E^-(\lambda)$ from Eq. (15) and $g_q = 1$, quartic reference] and for $\lambda \geqslant 0.2$,

$$g_q = (1 + 0.128\lambda^{-2/3} - 0.003\lambda^{-4/3})^2 \exp[-\beta(0.22\lambda^{-2/3} - 0.0052\lambda^{-4/3})]$$

Here again we note that the heat capacity in Eq. (17) for the large-λ regime as well as the energy eigenvalues involve corrections to the quartic oscillator.

Since explicit energy formulas for arbitrary n are only available for the $\lambda \geqslant 0.2$ regime, we have restricted our high-temperature analysis to this case. Having discussed the small-λ behavior of the heat capacity in our analysis of Fig. 1, we only note from this figure that the heat capacity for the large-λ regime is asymptotic to three-quarters. From Eq. (14) we see that the quartic-oscillator asymptotic limit of the heat capacity is 3/4, while in Eq. (6) the anharmonic oscillator approaches 3/4 as $(\beta/\lambda)^{1/2}$, which is seen in Fig. 1. Thus, as in the low-temperature cases, for $\lambda \geqslant 0.2$ at high temperatures the heat capacity approaches the behavior of the quartic oscillator.

We thus conclude that the thermodynamic properties of the anharmonic oscillator can be characterized by two λ regimes. For small λ (<0.2) the behavior is similar to that of the harmonic oscillator, while for large $\lambda(\geqslant 0.2)$ the behavior is analogous to that of the quartic oscillator. However, for both λ regimes at higher temperatures the thermodynamic properties tend toward those of the quartic oscillator through the contributions of the higher energy levels (quartic like) to the partition function, this becoming more significant for λ decreasing.

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